Temperature-Dependent Compensation And Optical Quenching By Thermal Oxygen Donors In Germanium

Dan M. Watson [1,2], Matthew T. Gupfill [1], James E. Huffman [3], Timothy N. Krabach [4] and S. Nicholas Raines [1]

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Abstract

Photothermal ionization spectroscopy of germanium, doped in the impurity-band conduction range with gallium acceptors and with thermal oxygen donors, reveals that the donors and acceptors compensate each other at temperatures higher than about 5 K but that the impurities coexist as neutral donors and acceptors at lower temperatures. At the lowest temperatures, optical quenching is observed for wavelengths where both impurities have transitions. These effects are used to infer a weak coupling between the neutral acceptor and donor states. The small strength of this coupling sets the thermal oxygen donor apart from all other shallow donors in germanium and silicon.

I. Introduction

Thermal oxygen donors (TODs) have been known and studied in germanium for more than thirty years. In most respects they are quite similar to the well-known TODs in silicon. These shallow impurities can be created in germanium crystals into which oxygen has been incorporated interstitially, by annealing the material at temperatures of 600-750 K and quenching from that temperature range. Higher-temperature processing can destroy the donors. That the impurities are double donors is established by Hall effect measurements [5] and deep level transient spectroscopy (DLTS) [6]. Far-infrared absorption spectroscopy [7] and photothermal ionization spectroscopy (PTIS) [6] show that the double donors have helium-like energy levels and transitions. The donors occur as a family; in a given sample, a superposition of several helium-like spectra is seen, each with a different ground-state binding energy in the range 14-18 meV [8]. The number of family members detectable depends upon the details of the high-temperature processing, and upon the thermal history at cryogenic temperatures. There are TODs, called bistable, for which rapid cooling to low temperatures is necessary for observation of their spectra. Very slow cooling, or cooling under illumination by bandgap radiation, inhibits these donors' optical and electrical activity [9]. Other members of the TOD family lack this property.

The family of TODs is generally thought to involve clusters of oxygen whose various sizes and configurations give rise to different ground-state energies. Studies combining far-infrared spectroscopy

[1]Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627-0171
[2]NSF Presidential Young Investigator.
[3]Rockwell International Science Center, 3370 Miraloma Avenue, Anaheim, CA 92803.
[4]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109
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and electron paramagnetic resonance [9,10,11] have revealed that the TOD wavefunctions are anisotropic. Some display C_{2v} symmetry, with {110} mirror planes and the two-fold axes along ⟨100⟩, similar to that inferred for silicon TODs; others have C_{3v} symmetry. However, the microscopic structure of the thermal oxygen donor in germanium is unknown, as is still the case in silicon.

We have recently found another interesting property of the thermal oxygen donors in germanium: although the donors compensate shallow acceptors at high temperatures, they do not do so at low cryogenic temperatures ($\lesssim 5$ K). A similar effect has been noted in silicon at low impurity densities [12,13], but has not attracted much attention. In our germanium samples, doped with TODs and with gallium at a density slightly below the metal-insulator transition, the donors and acceptors both appear to be neutral at low temperatures, even though in the same material some of the gallium acceptors are compensated by other residual shallow donor impurities, and even though there is appreciable overlap between the gallium impurity states and the TOD states. This is very different from the behavior of all other shallow impurities at low and high doping densities, for which the minority impurity is always completely ionized, as appropriate for the energy interval between their ground states and the Fermi level.

II. Experiment

We will discuss specifically results obtained on three samples, for which the fabrication and characterization are described more completely elsewhere [14,15]. Each sample is representative of devices taken from three wafers of Ge:Ga, 0.4 mm thick, with (100) faces and the same gallium concentration. For two of the samples, which we denote GO1 and GO2, oxygen was present in the atmosphere surrounding the crystal during growth, resulting in the incorporation of large concentrations ($> 10^{16}$ cm^{-3}) of interstitial oxygen. The other sample, denoted G1, has much less oxygen ($< 10^{12}$ cm^{-3}). On one face of each wafer, a 3.7 μm thick layer of intrinsic germanium was grown by chemical vapor deposition, using ultra-high-purity $GeCl_4$ as the germanium source and H_2 as the carrier gas. These layers are very pure, with net acceptor concentrations near 10^{12} cm^{-3}. Before the growth of the intrinsic Ge epilayers, the substrate wafers were given a one minute, 900 K dispersion anneal, and during growth were held at a temperature of 730 K for 15 minutes, activating the thermal oxygen donors in samples GO1 and GO2. All three samples were shown by spreading-resistance measurements to be p-type throughout at room temperature. The gallium concentration was measured to be 3.0×10^{16} cm^{-3} by room-temperature resistivity (before formation of TODs); the concentration of shallow donors besides oxygen was determined to be approximately 4×10^{12} cm^{-3} by cryogenic capacitance-voltage measurements [14]. Ohmic electrodes were created on each face of the structures by boron implantation. For the intrinsic-layer face, the implantation took place through a photolithographic mask, defining square active areas of the wafer; a small enough implant dose was used in this step that the resulting electrode is transparent at far-infrared wavelengths. The substrate-face electrode was coated with thin layers of tungsten and gold, and then fastened to a leadless integrated-circuit chip carrier with conductive epoxy. Electrical connection to the exposed, intrinsic-layer electrode was made with aluminum wires, ultrasonically bonded to the germanium surface.

The role of the intrinsic layer is to keep the noisy, parasitic current associated with impurity band conduction in the heavily doped sample from completing the circuit, thereby improving the signal-to-noise

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For photothermal ionization spectroscopy, the samples were operated in a pumped liquid helium Dewar [18], stabilized above the bath temperature in the range 1.5 K - 12 K through the use of calibrated silicon diode temperature sensors and an active cryogenic temperature regulator [19]. They are cooled from room temperature to low temperatures in the dark, in times short enough to expect the formation of bistable thermal oxygen donors as well as non-metastable ones. Photocurrent was amplified with low noise, cryogenic silicon JFET transimpedance amplifiers, also residing inside the Dewar. Light from a vacuum far-infrared Fourier-transform spectrometer [20] was focused on the samples, through a polyethylene Dewar window and a series of cryogenic filters that reject wavelengths shortward of 50 μm with attenuation factors in the range 10^{-4} - 10^{-5}; in particular, there was no bandgap radiation present. The signal spectrum was divided by that from a cryogenic Ge:Ga composite bolometer or a room-temperature pyroelectric detector, to remove the instrumental transmission function, and calibrated in terms of current responsivity (current per unit incident power) by scaling the spectra to match precise measurements of the current responsivity made using narrow-band filters set at λ = 88.4 μm and 166 μm. The current responsivity R (photocurrent per unit incident power) is proportional to the product of the quantum efficiency η and the average photoconductive gain G:

$$R = \frac{\eta G e \lambda}{hc} ,$$

where $-e$ is the charge of the electron, h is Planck's constant, and c is the speed of light. The photon flux was always low enough that the fraction of impurities photoionized was quite small (< 10^{-7}).

III. Experimental results

Figure 1 is a plot of the current responsivity as a function of frequency ($1/\lambda$) of all three samples, at T = 1.7 K and at a substantially higher temperature. At the lower temperature, the spectrum of each device is dominated by response from the gallium impurity. The two most prominent narrow features are the Ge:Ga D (68.05 cm^{-1}) and C (74.08 cm^{-1}) lines, which are analogous to the n = 1-3 and n = 1-4 transitions of an ideal hydrogenic impurity, and which are the strongest lines seen in PTIS studies of this impurity in germanium [21,22]. The Ge:Ga photoionization continuum begins at 89 cm^{-1}. At the higher temperature in the oxygen-bearing detectors GO1 and GO2, the spectrum of gallium is absent; instead, we see a dense collection of narrow features in the 100 - 140 cm^{-1} frequency range, and an ionization continuum at higher frequencies. Each of the strong narrow features corresponds to a 1s-2p_0 or a 1s-3p_0 transition of a helium-like thermal oxygen donor, which are the strongest lines in PTIS and absorption spectra of this impurity [6,7]. The wavelengths of TOD lines and continuum agree well with those obtained in earlier

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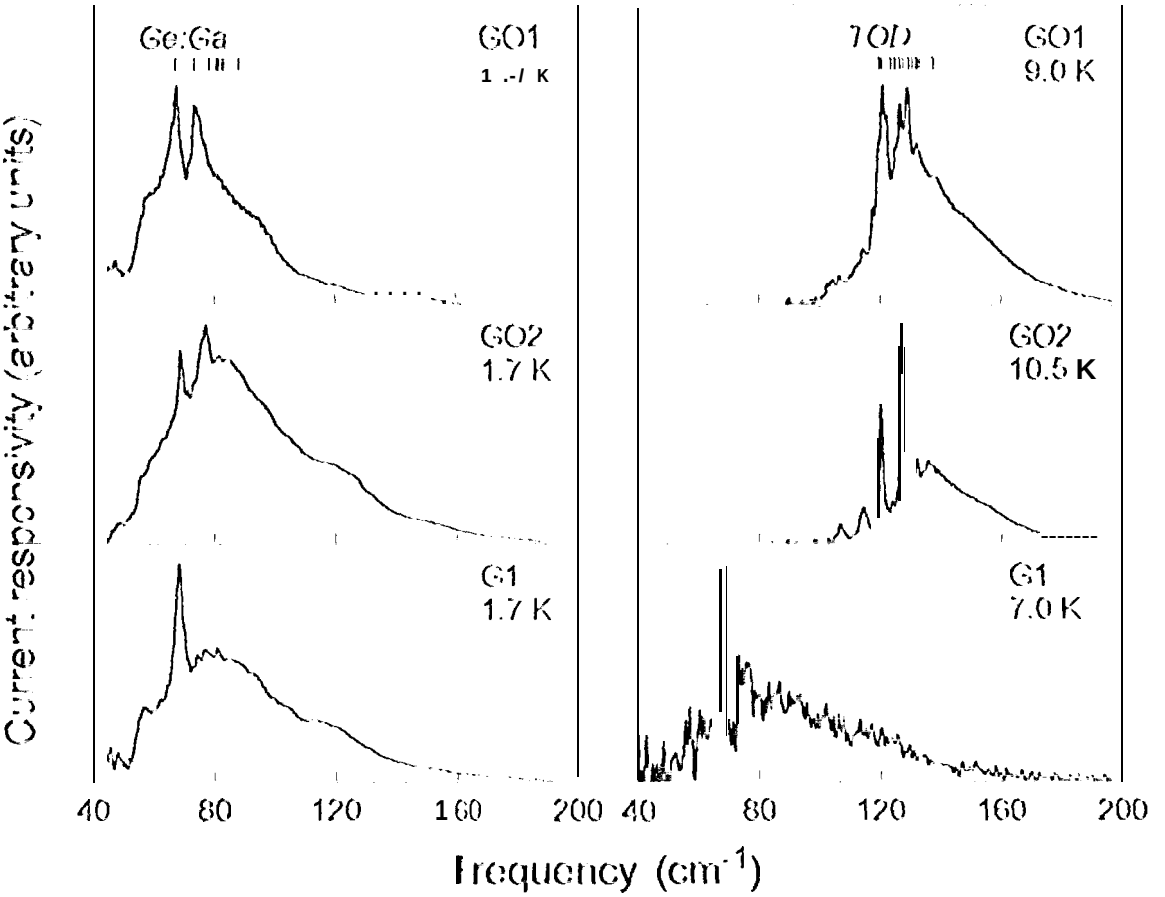

Figure 1: Current-responsivity spectra of the three samples at low and high cryogenic temperatures. The spectral resolution is 1 cm^{-1}, and the vertical axis of each frame has been scaled independently. Larger bias voltages were used in the lower temperature measurements (70 mV, peak electric field 100 V cm^{-1}) than at higher temperatures (5 mV, 13 V cm^{-1}). The positions of the hydrogenic transitions of Ge:Ga [21] are marked above the low-temperature spectra; those of the helium-like $1s$-$2p_{\pm}$ TOD transitions [8] above the high-temperature ones.

studies [8]. Figure 2 is a high-temperature spectrum of GO1 in which the measurements are compared in detail with TOD line wavelengths and identifications. Five different TOD spectra - *D* through *H*, in the nomenclature of Clauws and Vennik [8] - are clearly represented in the measurements by at least one $1s$-$2p$ or $1s$-$3p$ transition. Several lines are blended with stronger features, and are not seen unambiguously. Lines of the "later" TODs, for which longer annealing is required for formation, appear to be stronger than those of the "early" ones; donor *H*, for instance, dominates the spectrum of sample GO2. We have also detected several unassigned features in the 100-115 cm^{-1} range that appear in TOD absorption spectra [7], and two additional narrow features at 117.9 and 122.4 cm^{-1} (see Figure 2). Our high-temperature spectra do not show the weaker $1s$-$2p_0$ lines in the 85-100 cm^{-1} range; this is consistent with the sensitivity of the present measurements and previous PTIS spectra [6]. All of the response disappears rapidly as the temperature is raised above 11 K. From the quantum efficiency in the TOD ionization continuum at 140 cm^{-1} observed at $T = 7$ K, and a photoionization cross section derived at the same frequency and temperature from absorption measurements by Clauws and Vennik [7], we obtain a value of 1.5×10^{16} cm^{-3} for the total neutral TOD concentration in the active region of sample GO1, and 8×10^{15} cm^{-3} in GO2.

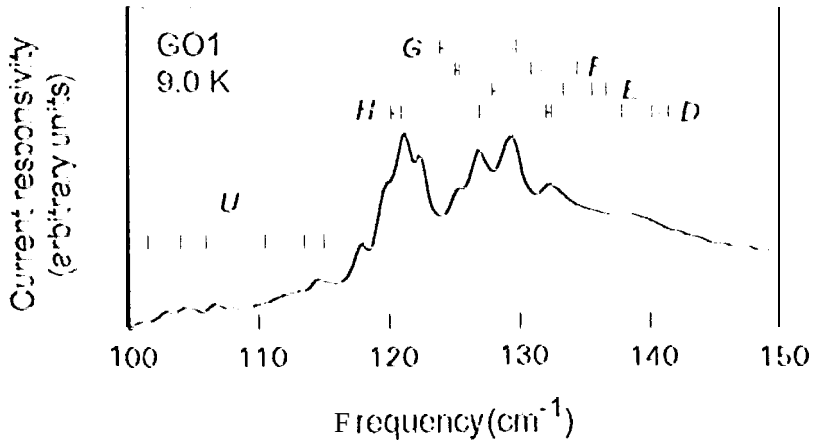

Figure 7. Current responsivity spectrum of sample GO1 at $T = 9.0$ K, with frequencies indicated as reported by Clauws and Vennik [8], for TOD transitions assigned to donors *D*-*H* and several unassigned transitions (*U*). The bias voltage is 5 mV (peak electric field 13 cm^{-1}), and the spectral resolution is 1 cm^{-1}.

At intermediate temperatures in the oxygen-bearing samples, the spectral features of both impurities are seen, as is illustrated in the current responsivity spectra of sample GO2, shown in Figure 3. The appearance of their features in these spectra is a unique attribute of the TODs. Transitions of other shallow donors, as minorities, would be visible only if the sample were illuminated continuously with bandgap radiation, which neutralizes the compensation; however, in the present case, no bandgap radiation was present. This shows directly that TODs and gallium coexist as neutrals at low temperatures. As temperature increases, the TOD response increases, and the long-wavelength gallium response decreases smoothly. The Ge:Ga photocurrent disappears at temperatures above 6.0 K.

Ge:Ga samples without oxygen behave quite differently. Included in Figure 1 is the current-responsivity spectrum of the oxygen-free sample G1 at $T = 7.0$ K, the highest temperature at which we could detect the spectrum of this device. All of the response is due to Ge:Ga; there is no evidence for the TOD spectrum. At this temperature the features of Ge:Ga are undetectably small, and those of the TODs quite strong, in samples GO1 (see Figure 1) and GO2 (Figures 1 and 3).

We made a more detailed comparison of the temperature variation in the range 1.8 -5.5 K for the current-responsivity spectrum of GO1 and G1, two samples that, apart from their oxygen content, are similar in all of their low-temperature properties. The results are illustrated in Figure 4. As temperature increases from the lowest values, the response of G1 due to the long-wavelength Ge:Ga lines increases continuously, while the Ge:Ga ionization continuum response peaks near $T = 3$ K. The decrease in ionization-continuum response for temperatures above 3 K represents the onset of thermal ionization of the Ge:Ga centers. In the oxygen-bearing sample GO1, the Ge:Ga lines increase in strength less rapidly, and the ionization continuum begins to decrease in strength at a lower temperature. Figure 5 contains a plot of the current responsivity in the two samples in the Ge:Ga *D* line (68.05 cm^{-1}) and at the Ge:Ga ionization threshold (labeled 1, 89 cm^{-1}), showing that the Ge:Ga response in GO1 is weaker at 5.0 K than at 2.0 K, relative to G1. This additional decrease is likely to be due to the activation of compensation by the thermal oxygen donors, as we will now demonstrate. The quantum efficiencies of GO1 and G1 are less than 0.2 over the whole range of frequency and temperature explored. For frequencies below the TOD threshold, but above the Ge:Ga ionization threshold, we can therefore write

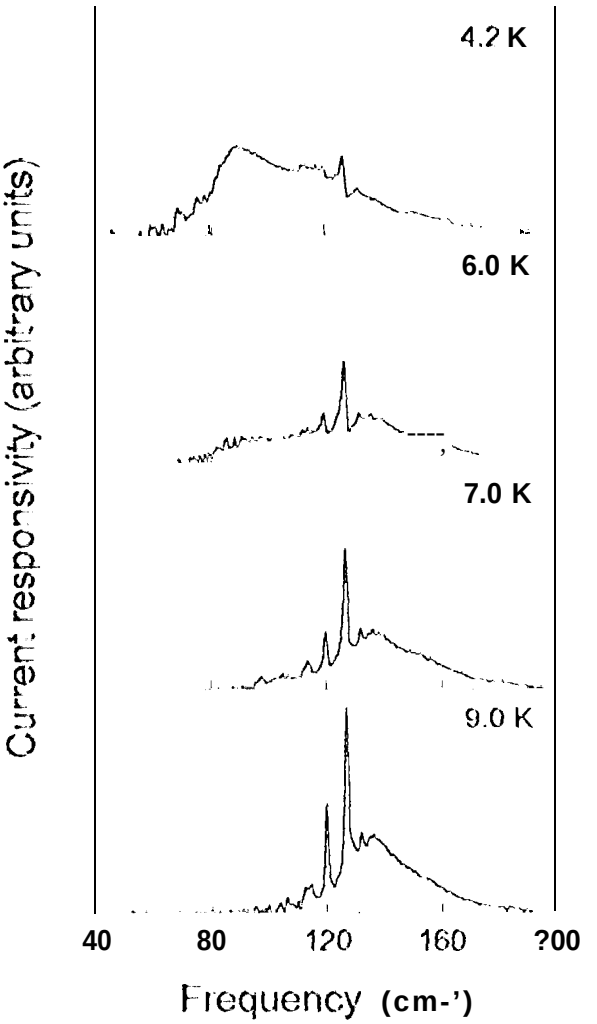

Figure 3: Current responsivity spectrum of GO2, over a range of temperatures at a constant voltage bias of S mV (peak electric field 13 V cm^{-1}). The vertical scale is the same for all the frames, and the spectral resolution is 1 cm^{-1}.

$$\eta = n(\mathrm{Ga}^0)\sigma_I \ell \eta \ , \qquad (?)$$

where $n(\mathrm{Ga}^0)$ is the density of neutral gallium impurities in the ionized-impurity depletion region, σ_I is the photoionization cross section at the frequency of interest, ℓ is the width of the ionized-impurity depletion region, and is the transmission of the front surface of the sample, which comes out to 7 = ().6S at the germanium refractive index, 3.92. A similar expression can be written for the quantum efficiency at the frequency of a Ge:Ga line, with of replaced by the product of a photoexcitation cross section $\sigma_{I'}$ and a field-assisted thermal ionization probability $P_f(T)$. The depletion-region width .! is determined by the bias electric field and the density of immobile ionized donors, and is constant in the measurements shown in Figures 4 and 5. The effective cross sections o, and $\sigma_{I'}P_f(T)$ arc properties of single impurities, and therefore vary in the same way with temperature for the two samples. The fionl-surface transmission 7 is, of course, the same for the two samples, and independent of temperature. Thus the ratio of the quantum efficiencies of the samples, or equivalently the ratio of current responsivities, gives the ratio of $n(\mathrm{Ga}^0)$. We have computed this ratio as a function of temperature, using current responsivity measured at the

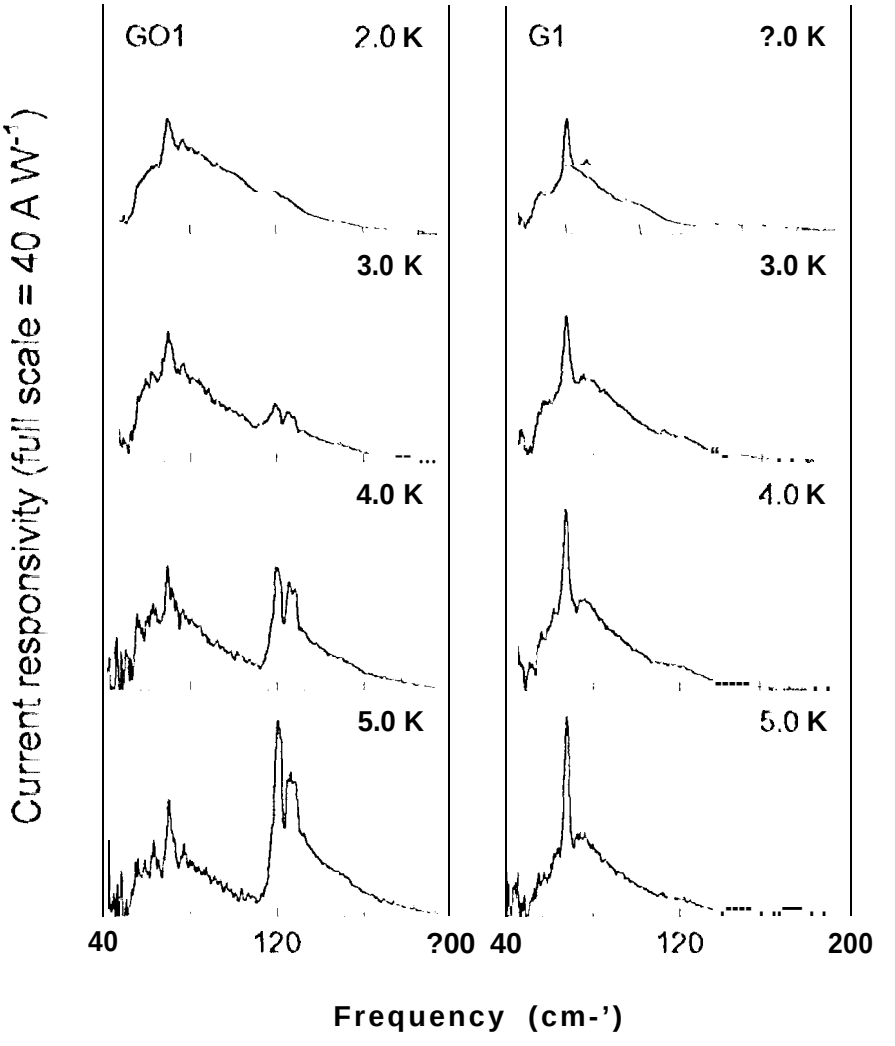

Figure 4: Cur tent responsivity spectra for oxygen-bearing sample GO1 and oxygen-free sample [i]. from ? K to 5 K. The peak electric field in the samples is constant al 135 V cm^{-1}, and the spectral resolution is 1 cm^{-1}, The vertical scale is the same for all flames, with full scale corresponding to a current responsivity of 40 A W^{1},

frequencies of the Ge:Ga ionization edge anti in the Ge:Ga *D* line; the results arc plotted in Figure 5, Relative to the oxygen-frw sample G1, the neutral gallium density in the oxygen-bearing sample GO1 declines by a factor of about two as temperature increases from 2 K to 5.5 K, and this may bc ascribed to compensation by the TODs.

A t the lowest temperatures, there is a steep decrease in the current responsivity of most heavily TOD-doped sample, GO1, above approximately 85 cm^{-1}, as can be seen in Figure 1, The decrease corresponds to the range of frequencies of the TOD transitions, and is not matched by the more. lightly TOD-doped sample GO2, nor the Oxyf;cll-flee sample G], nor by GO1 itself at higher temperatures, as shown in Figure 4. This effect is illustrated more clearly in Figure 6, where we plot the ratio of current responsivity spectra for the two oxygen-bear ing samples to that of sample (i 1, We interpret this result as *optical quenching*, or "negative photoconductivity," in the spectrum of sample GO1. In this dm'ice, neutral gallium acceptors and thermal oxygen donors, are available for photoionization. The '] TODs can be ionized

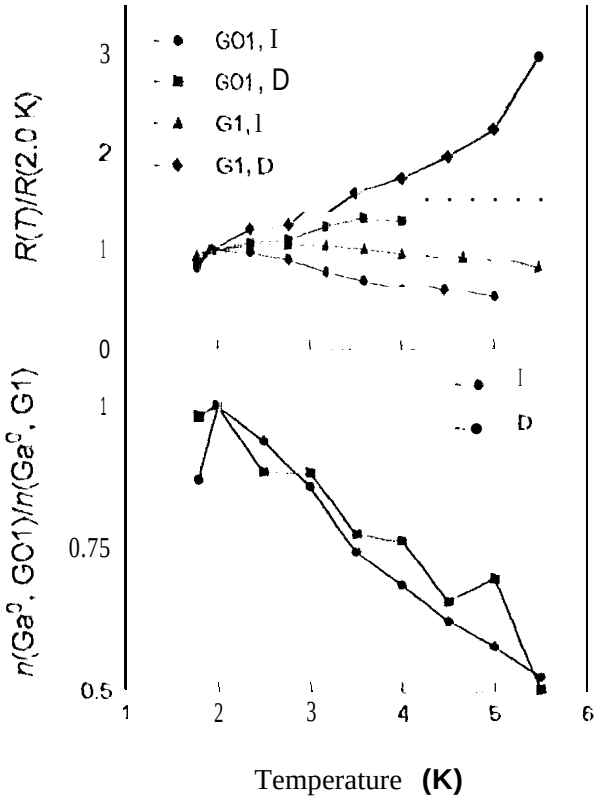

Figure 5. Upper panel: current responsivity as a function of temperature for samples GO1 and G1 at the wavelength of the Ge:Ga photoionization edge (f, 89 cm^{-1}) and the Ge:Ga *D* line (68.04 cm^{-1}), normalized 10 their values at $T = 2.0$ K. Lower panel: ratio of neutral gallium impurity density in GO I and G]. as a function of temperature.

directly for photon energies greater ihan 14-18 mcV, or *via* two step photothermal ionization processes (the Poole-Frenkel effect) for photons that can excite a helium-like transition of a TOD. Since the concentrations and cross sections arc compa t able, recombination of the resulting holes and electrons results in a smaller photocurrent than would be obtained in the absence of one impurity or the other, over the frequency range for which both can be photoionized The effect is not seen in GO2 because of its smaller concentration of TOI)s, Optical quenching is often invoked to explain the "reversal" of photoresponse features duc to minority impurities in PTIS experiments for which the compensation is neutralized by bandgap-light illumination of the sample [2],22 . in the present case, the optical quenching cor **responding** to the helium-]ikc TOD transitions is a collection of broad features covering the range of the transitions, as is often the case in field-as$isicd transitions. This **helps** distinguish the effect from a photothermal ionization process, such as that giving rise to the TOI) lines at higher temperatures, or simply from photoexcitation of 'I '1)]) levels followed by phonon **emission; boih** of these mechanisms give rise to sharp lines,

IV. Discussion

Ii is almost axiomatic that a shallow minority impurity in germanium is completely ionized at low temperatures. The capture of such bound car t iers by majority impurity centers pr oceeds through allowed transitions, **usually** involving mid-gap states of other impurities, and is expected and observed to be quite rapid and effective. However, i n our samples (IIC thermal - oxygen donors remain neutral even for

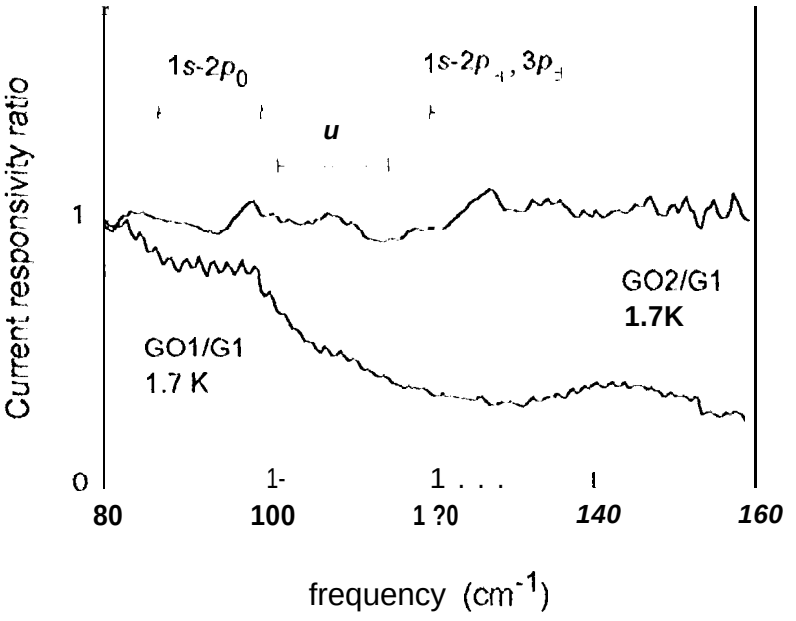

Figure 6: Ratio of current responsivity spectra from Figure 1, compared to the positions of the $1s - 2p_0$, IS- 2/1, , $1s - 3p_{+1}$, and unassigned transitions of the thermal oxygen donor S [8]

temperatures such that though their ground states lie above the Fermi level by energies that greatly exceed kT. This is especially surprising if one considers the large doping densities involved for gallium rind TOD impurities: donor and acceptor wavefunctions have substantial overlap among themselves and with each other. It would appear that the transitions resulting in capture by shallow acceptors are peculiarly weak, perhaps even forbidden, for electrons bound to thermal oxygen donors, a fact that is potentially of importance in the understanding of the structure of TODs. 1 n this picture the observed thermally activated compensation would take place as follows: the TOI)s and gallium impurities arc both ionized by phonons, producing electrons and holes that thermalize in the conduction and valance bands, recombine in the usual fashion, with the outcome that electrons arc. transferred from the donors to the acceptors.

At temperatures low enough to reduce substantially the mobility of carriers in the valence or conduction bands, it may bc expected in the present oxygen-bearing devices that recombination of free holes and electrons would become especially efficient. At frequencies for which excitation of both gallium acceptors and thermal oxygen donors is possible, this recombination would bc characterized by optical quenching: reduction of the photocurrent compared to lower- frequencies, or compared to the same frequencies at somewhat higher temperatures. This effect, which is evident in the spectrum of device GO1 (Figures 1 and 6), would bc an additional consequence of the lack of strong coupling between neutral '1'01) states and neutral gallium-impurity states.

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